Polyamines as a Potential Biosignature for Future Extraterrestrial Missions

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AbSciCon

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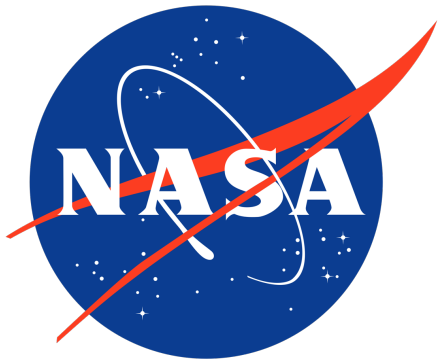
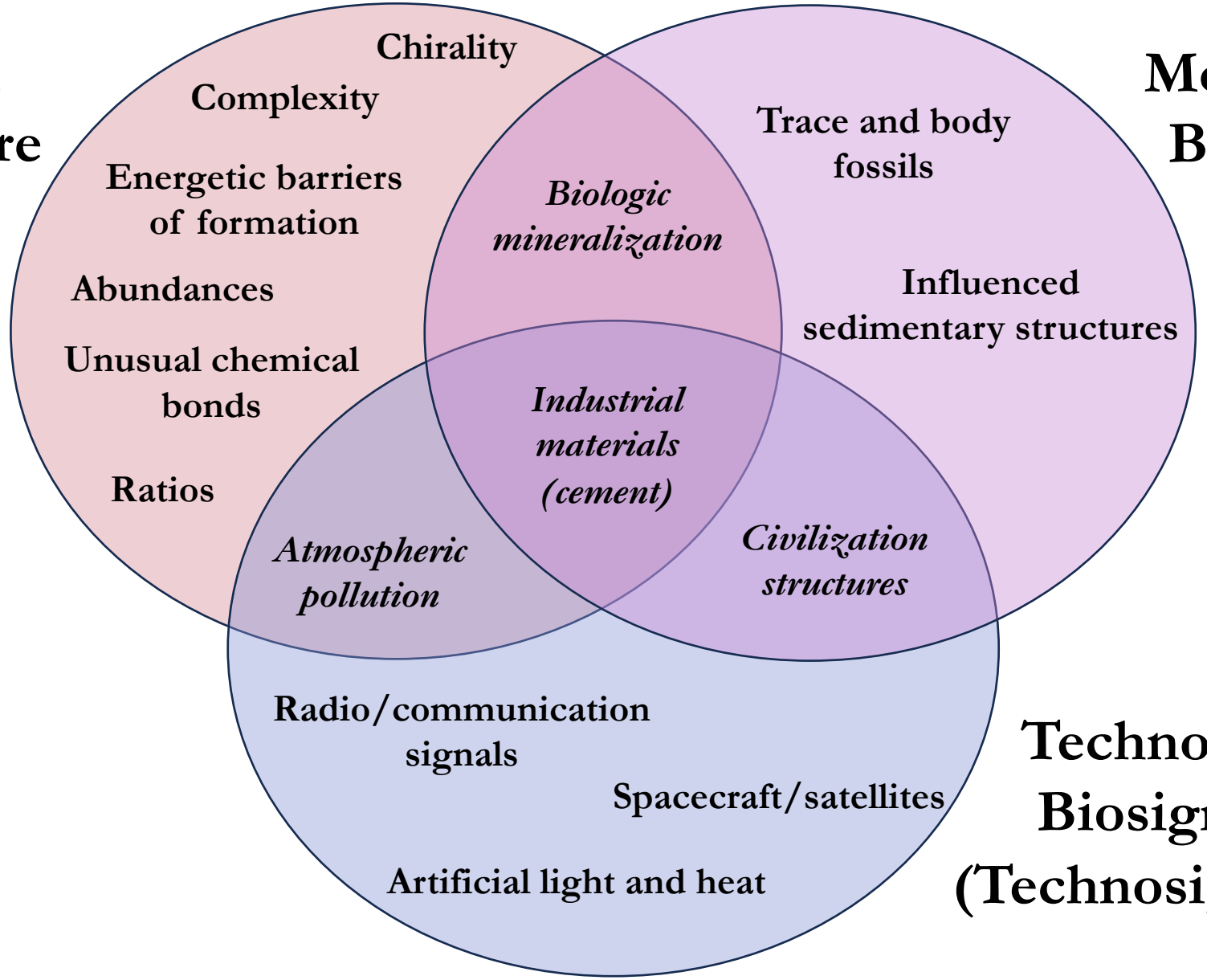
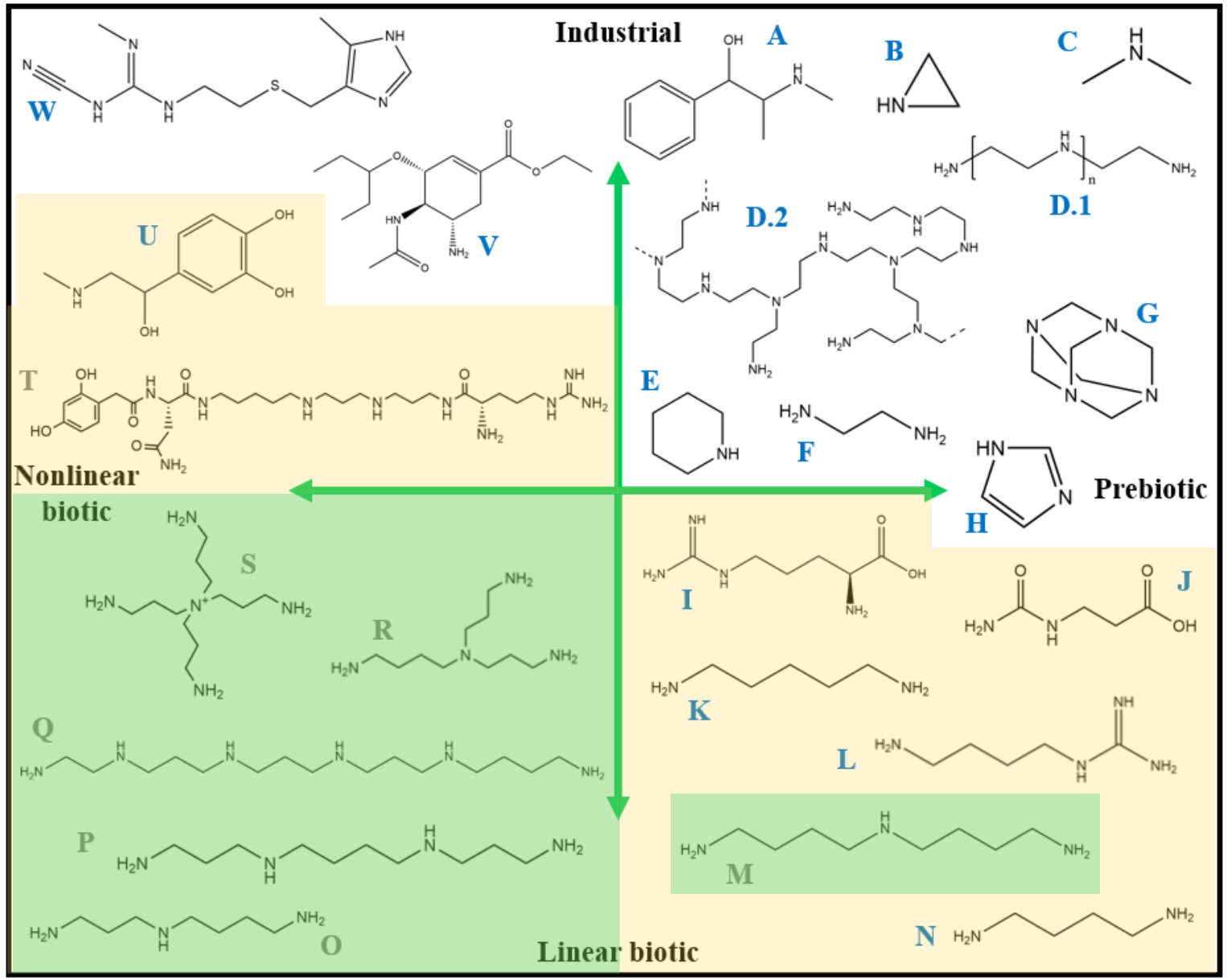


Types of biosignatures

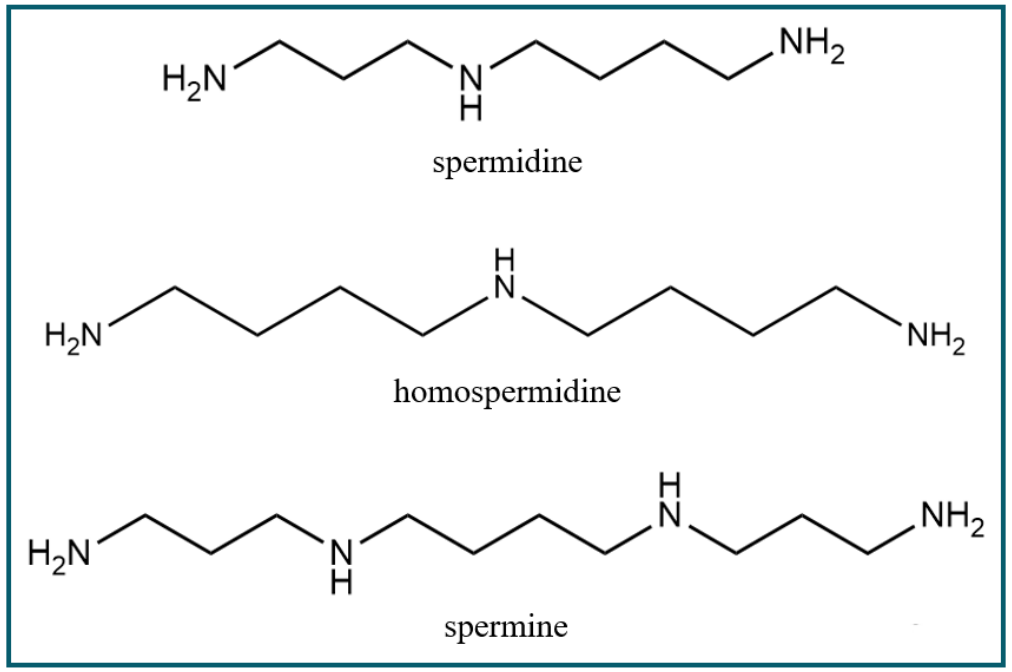


Diversity in di- and secondary amines



- Cartoon notational representation of N-bearing molecules
  - Category divides are a gradient
  - About half are made biologically
- What makes a polyamine?
  - We will limit the development of polyamines as a biosignature to **higher order alkyl polyamines (HAPs).**

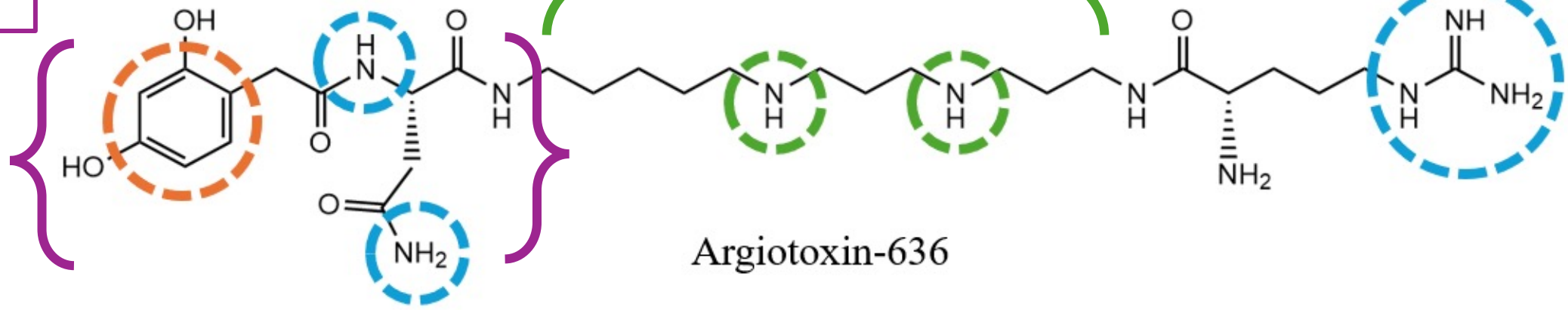
Biology of polyamines



- Virtually every organism is reliant upon polyamines for survival.
  - Found in all 3 domains of life (archaea, eukaryotes, bacteria)
  - Small, cationic molecules normally made with charged S-adenosylmethionine (SAM)
  - Wide range of functions: DNA/RNA stability

HAP core

complexity

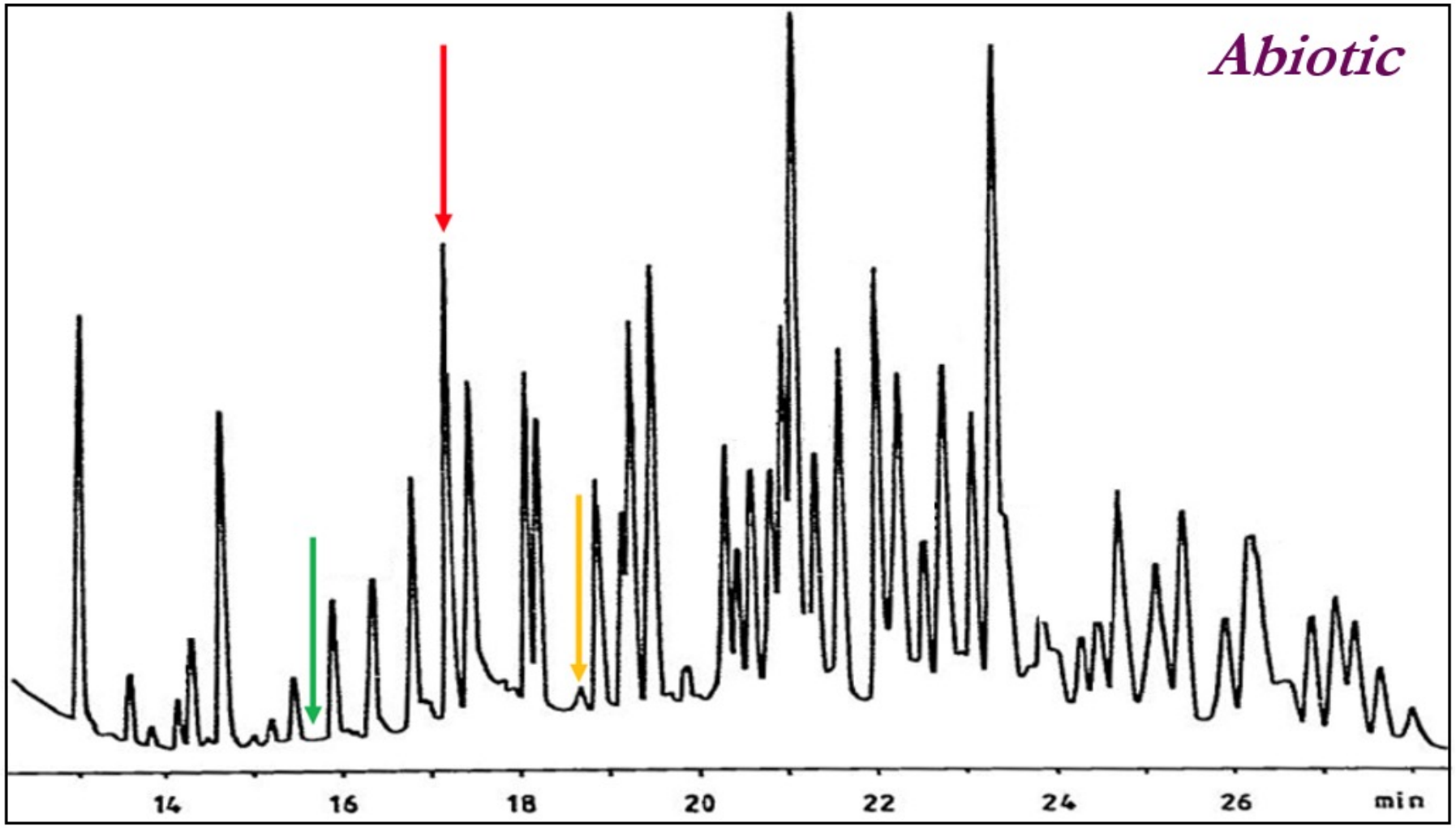


Motivating Question: Are polyamines a strong biosignature candidate to develop for future missions?

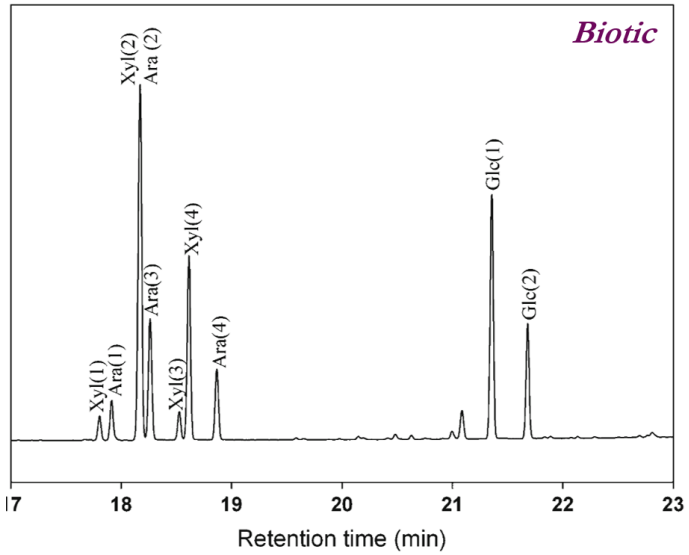
Hypothesis: HAPs cannot form under prebiotic conditions.

Alternative hypothesis: HAPs form in very low concentrations under prebiotic conditions along with a large disarray of related amines.

Untangling biotic from the abiotic



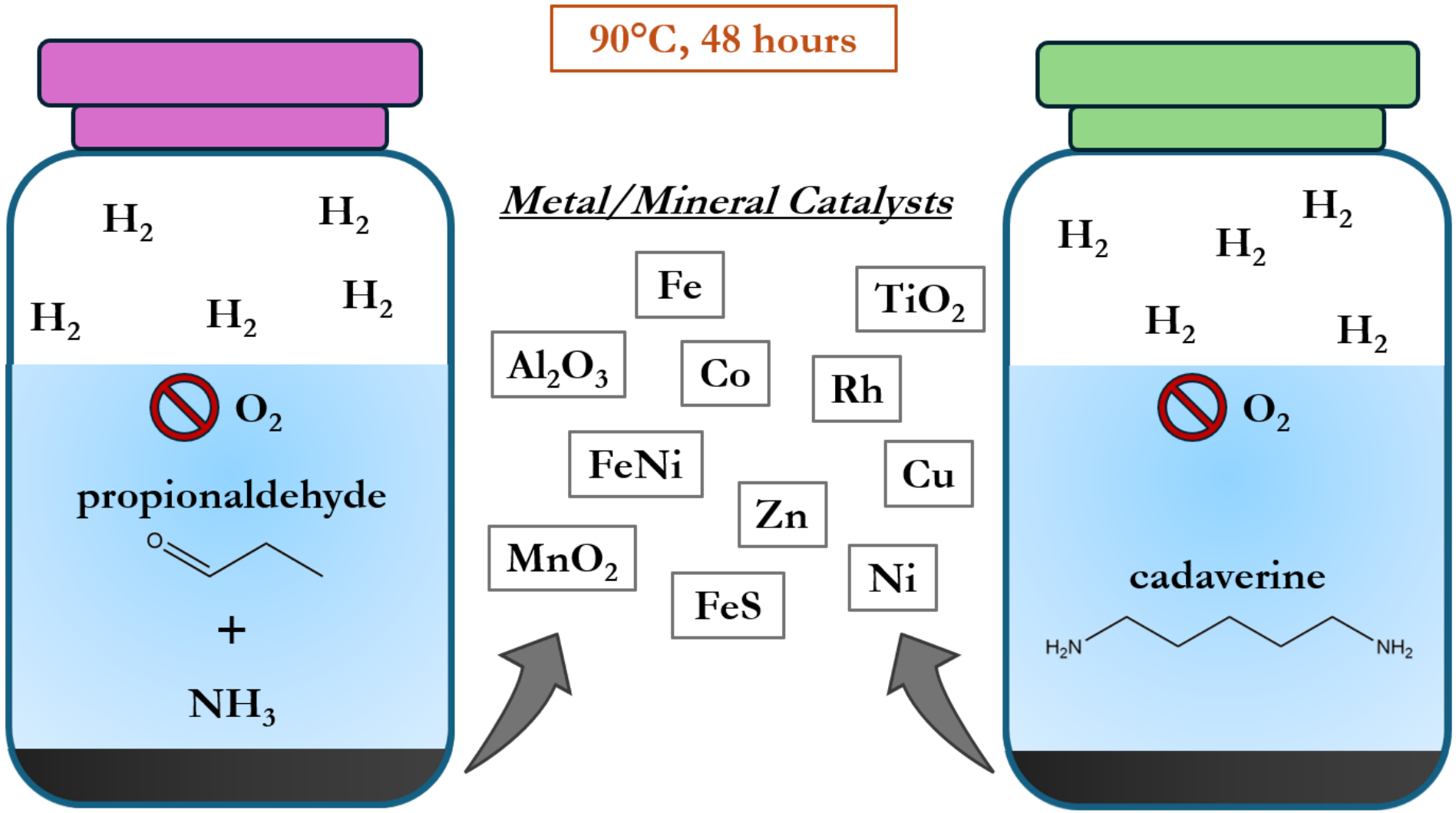
Decker et al., (1982)

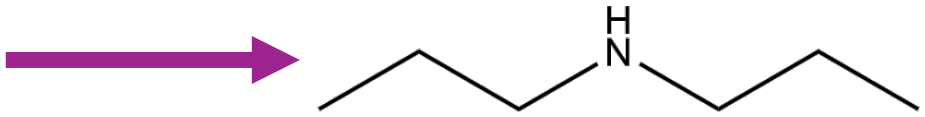


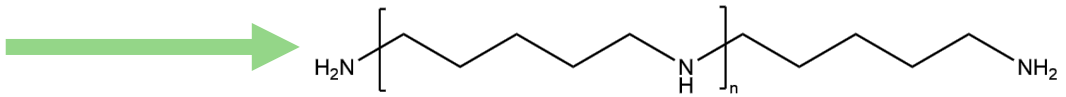
Sárossy et al., (2012)

- **Knowing how to pick out a biosignature amongst the mess of abiotic products will aid in identifying less obvious biosignatures that may not be "telltale signs".**

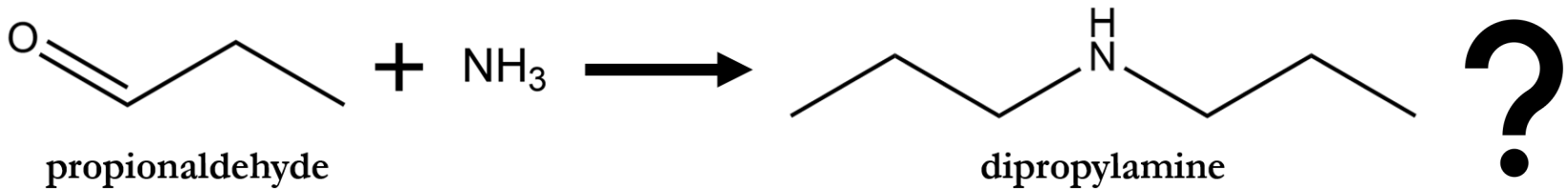
Proposed prebiotic HAP formation



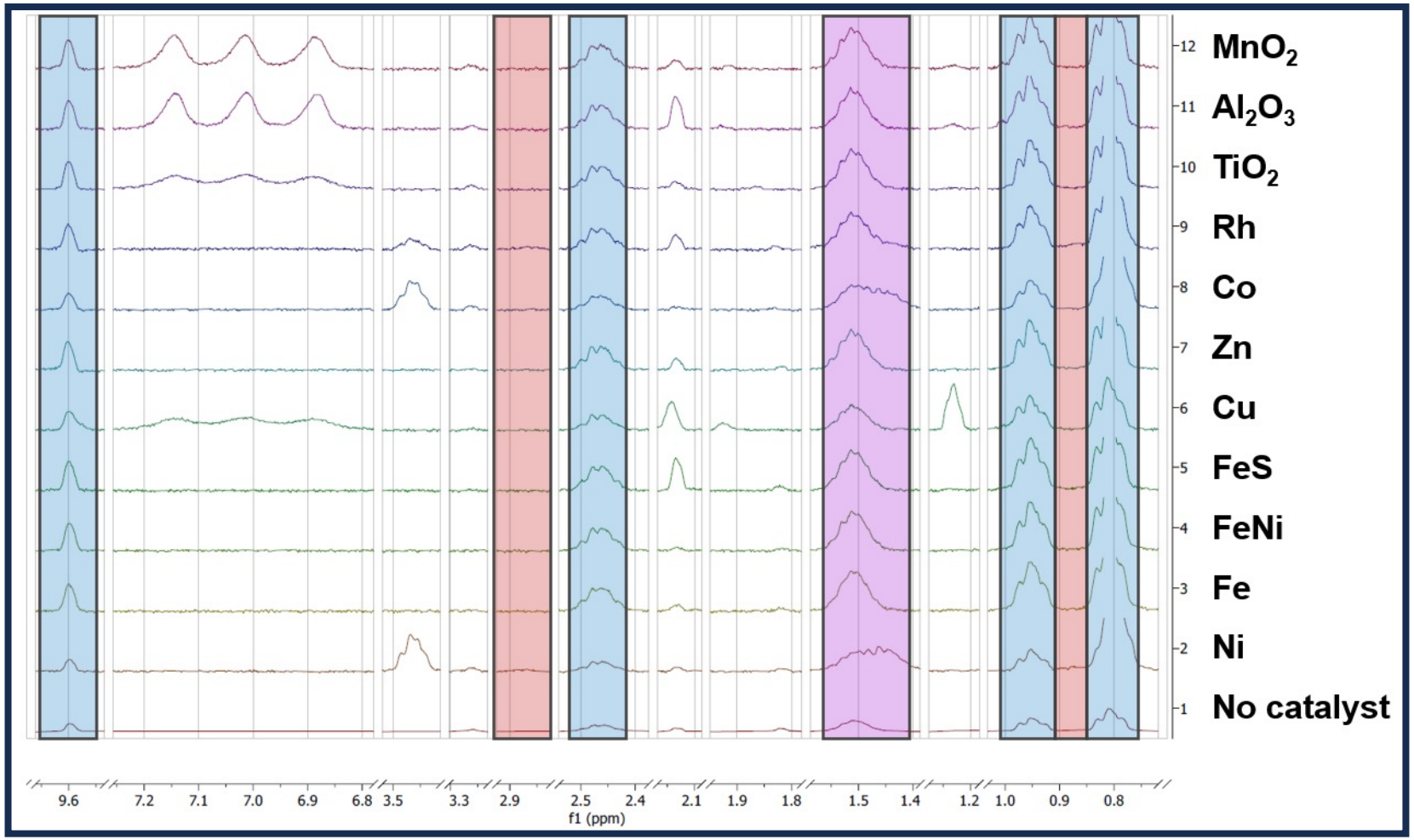




Prebiotic HAP formation



propionaldehyde dipropylamine



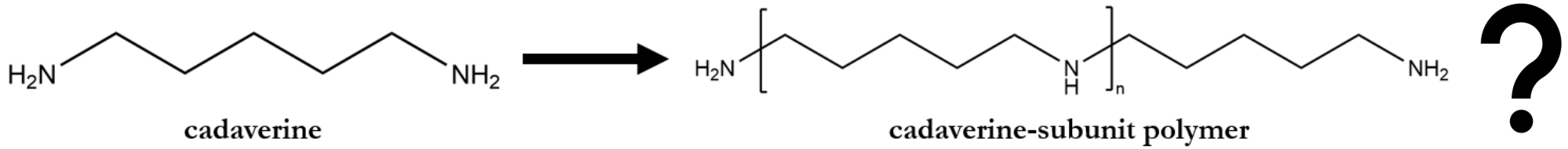
Propionaldehyde

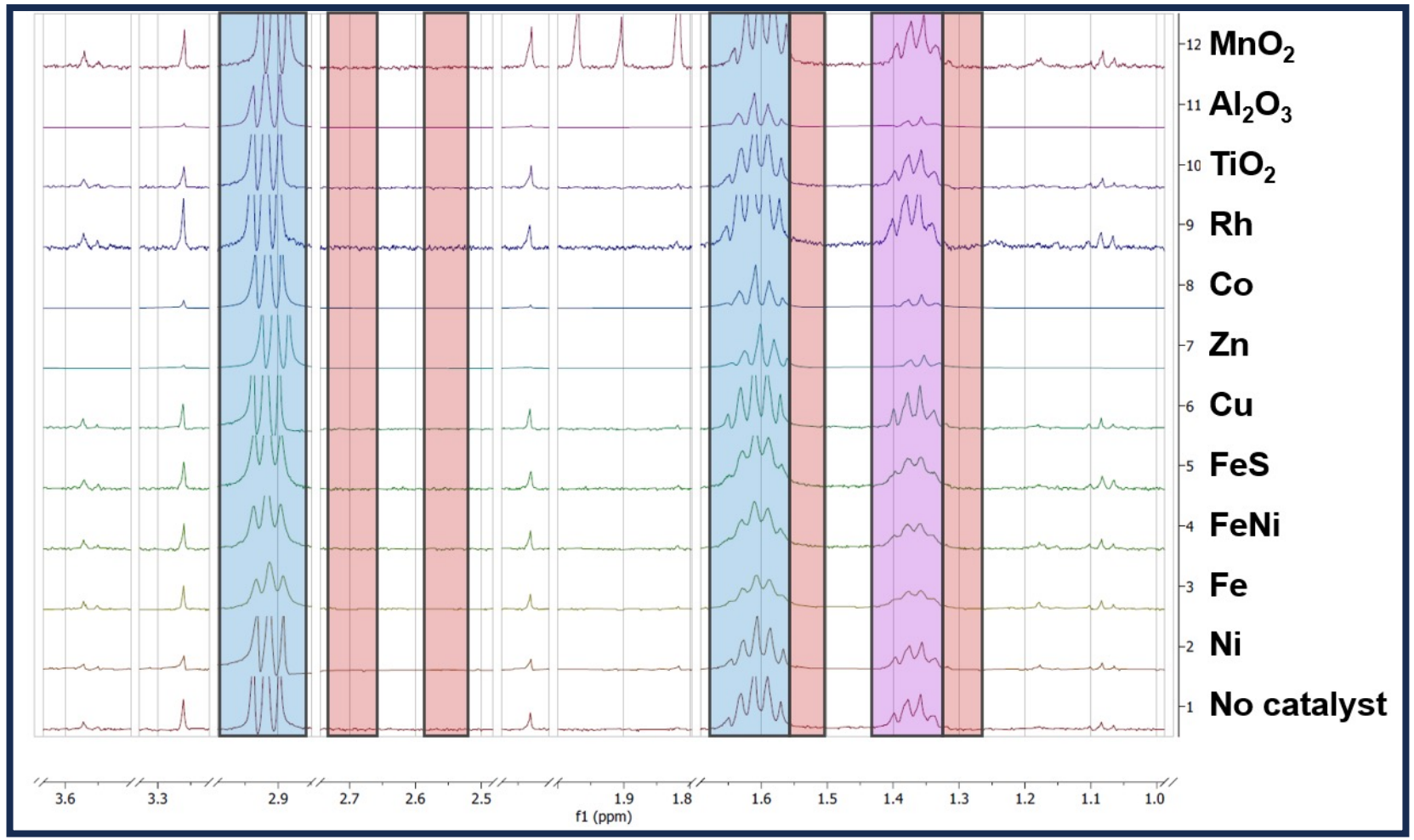
Dipropylamine

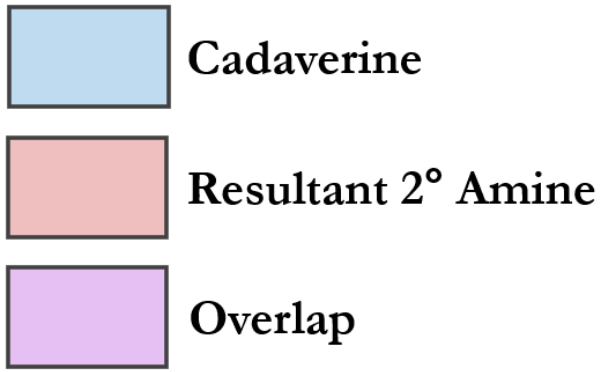
Overlap

- Initial propionaldehyde experiments do not show secondary amine formation.
  - ^{1}H-NMR for compound identification

Prebiotic HAP formation







- Initial cadaverine experiments do not show secondary amine formation.
  - ^{1}H-NMR for compound identification

Conclusions

- **We have identified polyamines as a potential chemical biosignature candidate for future extraterrestrial missions.**

- **Development of polyamines as a biosignature:**
  - Narrowed down "polyamines" to the specific **higher-order alkyl polyamines (HAPs)**

- **Prebiotic formation of HAPs:**
- HAPs do not show formation in initial prebiotic experiments.
  - 2x different starting compounds, 11x different metal/mineral catalysts
    - Lack of formation with a single aldehyde (propionaldehyde)
    - Lack of formation with a diamine (cadaverine)

Future directions

- **Investigate prebiotic HAPs in more detail to rule out as many possible prebiotic reaction schemes.**
  - Exploration with more identification methods
    - Gas chromatography mass spectrometry (GC-MS), flame ionization (GC-FID)
  - Exploration with more starting reactants
    - Single amines, dialdehydes, N-heterocycles (ring opening)
  - Exploration with other experimental conditions
    - Wet-dry cycling, spark discharge, low temperature, irradiation, pH, salinity

- **We hypothesize that polyamines are ancient and arose early in life before LUCA.**
  - We have begun to construct combined bacterial, archaeal, and eukaryotic phylogenetic trees for polyamine synthesis genes.
  - Answer the following questions:
    - What is the diversity and distribution of polyamine synthesis genes?
    - Which organisms lack polyamine dependence?
    - Which polyamines are the most ancient to life?

Thank you for listening!

Questions?

- *Miranda Sturtz*
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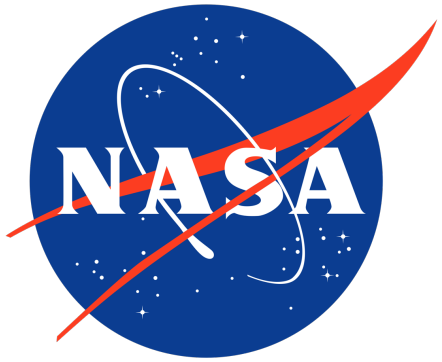

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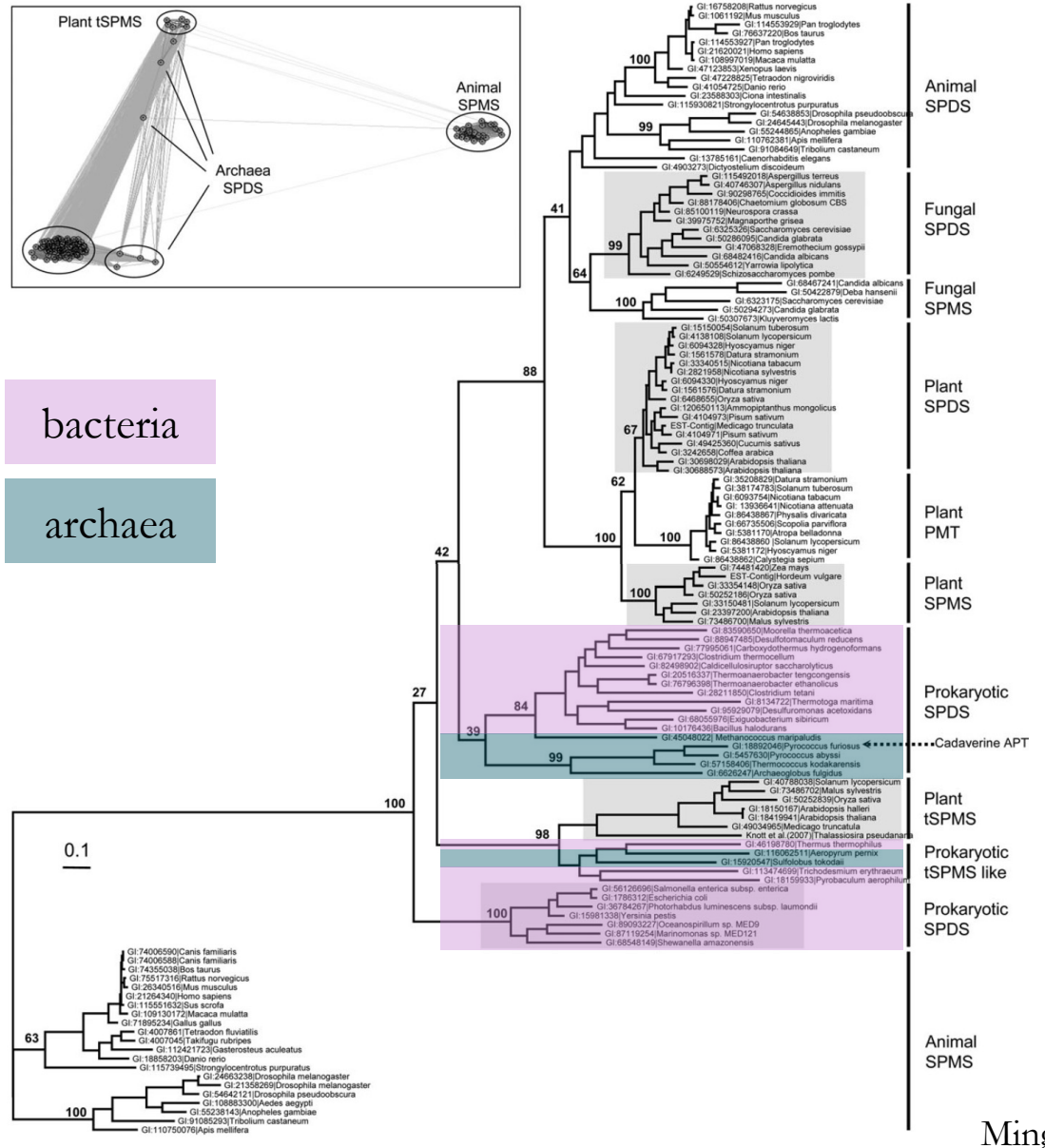
EXTRA: Universal dependence of HAPs?

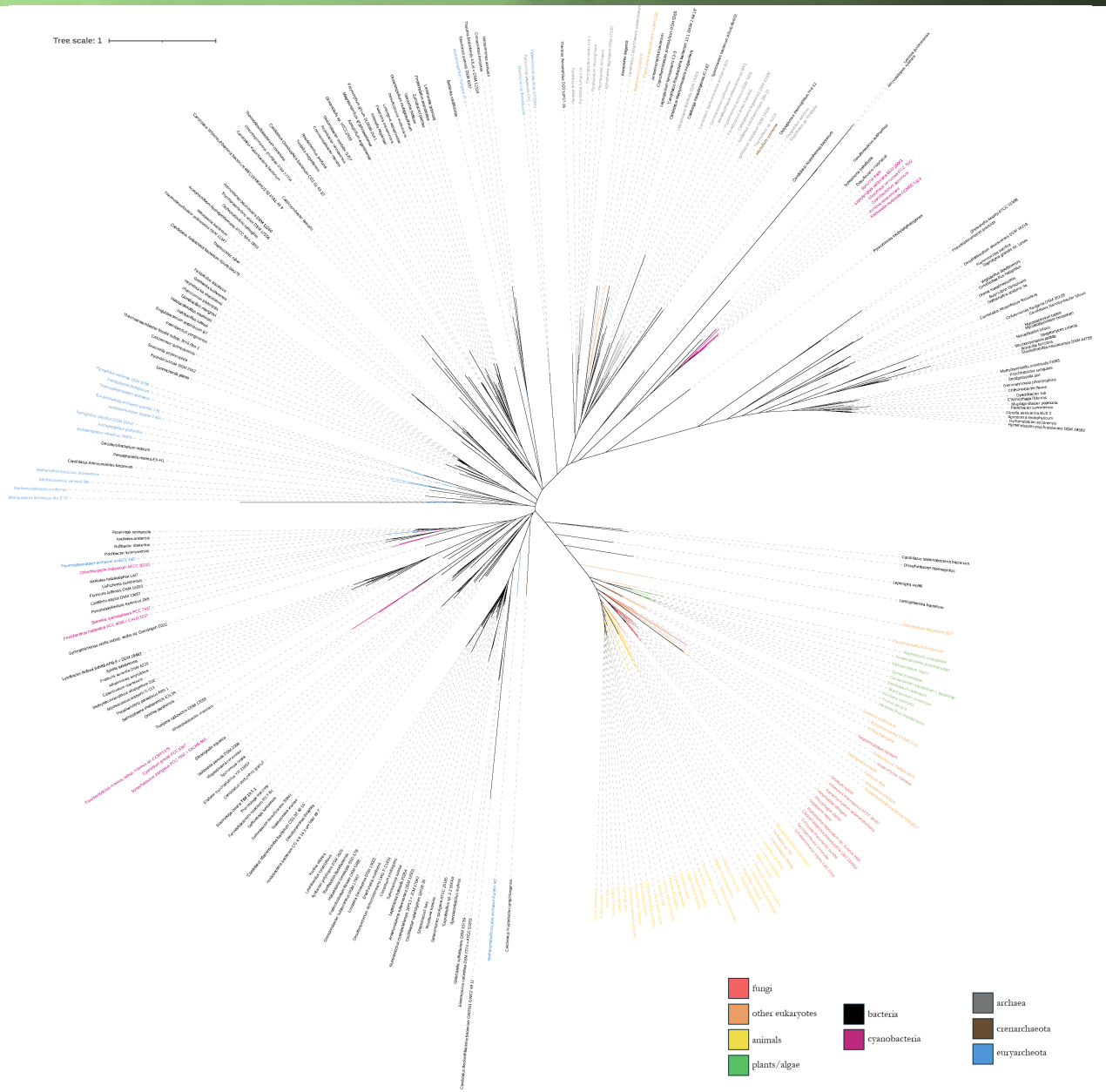


- While it is agreed overall that *most* organisms rely upon polyamines, some extremophiles have been debated
  - Not much research has looked at these organisms in depth beyond saying if they have polyamines or not, and most are outdated studies
    - Major lack of archaea and extremophilic bacteria
    - Lack of studies with non-plant/animal/fungus eukaryotes
  - New information and techniques are available to explore if they truly don't require polyamines, and when this adaptation arose

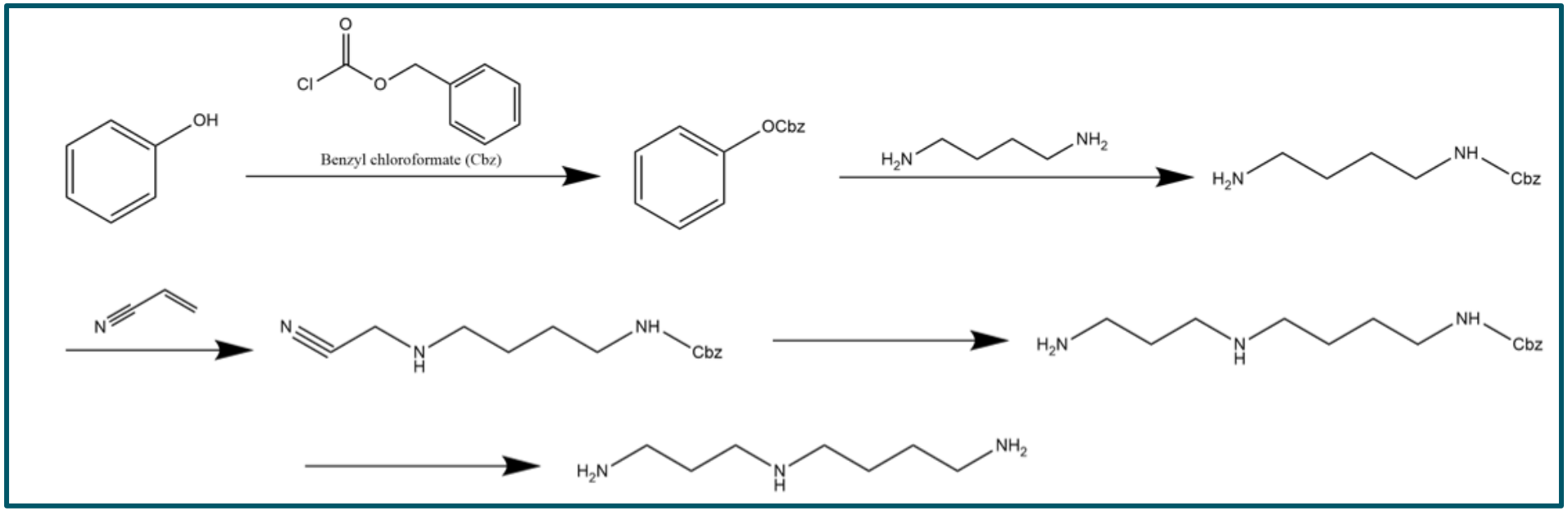
Minguet et al., (2008)

EXTRA: Universal dependence of HAPs?

- What is the diversity and distribution of polyamine synthesis genes?
  - Publicly available BLAST sequences
  - Here, specifically look at the simplest HAP- spermidine synthase.
    - Annotated as spermidine synthase but much variety in length of genes and confidence in proper IDing
  - Determine what the gaps are where organisms are missing the spermidine synthase (or other polyamine synthases).



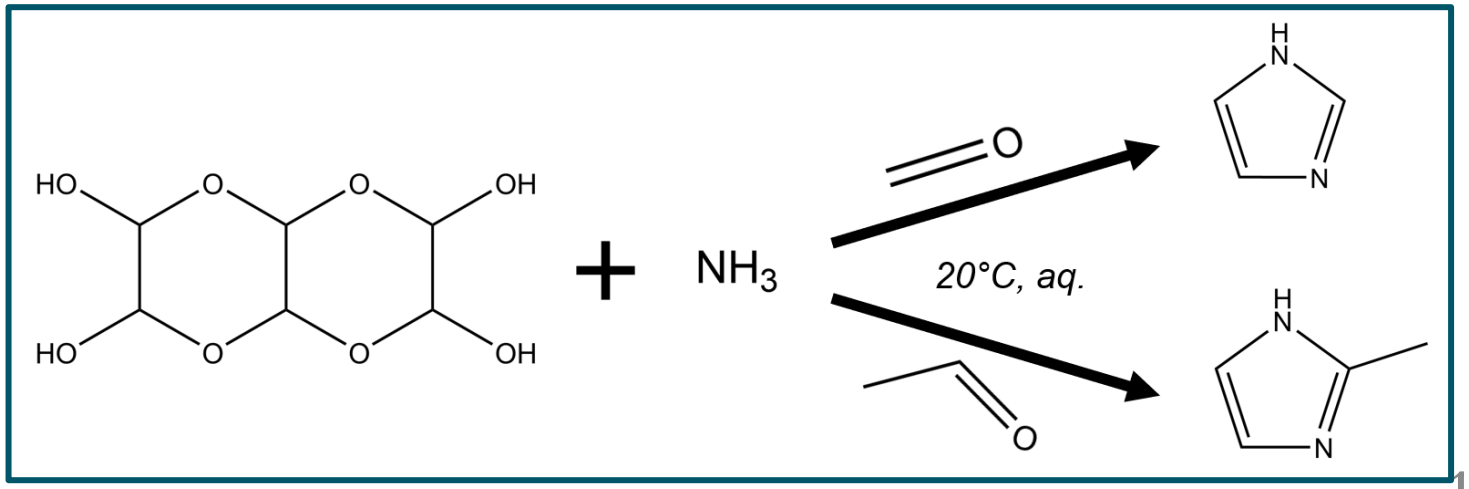
EXTRA: Abiotic/Prebiotic amine formation



- Major reactants of the industrial synthesis process of spermidine with secondary amine intermediates
- Highly unlikely to be prebiotic

Tianjin Pulaike Pharmaceutical Technology Co. Ltd.

- Prebiotic synthesis of imidazole and 2-methylimidazole
  - Not true secondary amine structures, or HAPs (N-heterocyclic ring formation instead)



Oró et al., 1984

EXTRA: NMR compound standards